



Fabrication and Study of Structural, Optical and Electrical Properties of UV curable Conductive Polyurethane Acrylate Films Containing Polyaniline-Co₃O₄ nanocomposites

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ARTICLE INFO

Article history: Received: 15 Dec 2015 Final Revised: 03 Jan 2016 Accepted: 17 Jan 2016 Available online: 17 Jan 2016 Keywords: UV cure Urethane acrylate Polyaniline Electrical conductivity

ABSTRACT

n this study, novel UV curable conductive nanocomposites containing urethane acrylate (UA) and polyaniline (PANi)-Co₃O₄ nanocomposites were fabricated. At first, PANi-Co₃O₄ nanocomposites have been synthesized with different molar ratios of aniline: Co_3O_4 nanoparticles by in situ chemical oxidative polymerization method of aniline using ammonium persulphate as an oxidizing agent. Afterward, PANi-Co₃O₄ nanocomposites were dispersed in UA matrix and cured by UV irradiation. Structural, optical properties, electrical conductivity and morphological characteristics of the nonocomposites were analyzed by FT-IR and UV-Vis spectroscopy, electrical conductivity measurements and scanning electron microscopy (SEM), respectively. FT-IR, UV-VIS spectra offered the information about chemical structure of the products. The SEM images of the PANi-Co₃ O_4 nanocomposites showed uniform distribution of Co_3O_4 nanoparticles in PANi matrix. Also SEM images of the PUA-PANi-Co₃O₄ nanocomposites films showed distribution PANi-Co₃O₄ nanocomposites in PUA matrix. Electrical conductivity measurements of PANi- Co_3O_4 nanocomposites revealed that the conductivity of PANi decreased with adding Co_3O_4 nanoparticles in contrast to the conductivity of PUA which increased with adding PANi-Co₃O₄. Prog. Color Colorants Coat. 9 (2016), 41-52 © Institute for Color Science and Technology.

1. Introduction

Conducting polymers have attracted attention in recent decades because of their potential applications in different fields such as super capacitors, rechargeable batteries, chemical sensors, corrosion inhibition and

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microwave absorption [1-3]. Polyaniline (PANi), as an appropriate conducting polymer, has attracted a considerable interest in recent years because of its suitable electrical, optical, and electrochemical

properties as well as its high stability [4-8].

Polymer nanocomposites are obtained by combination of polymers and organic-inorganic fillers at the nanometer scale. Organic-inorganic nanocomposites have received greater attention in recent years due to thier interesting possibilities for structural modifications and thier promising potential applications in chemistry, medicine and biology. A wide range of organic and inorganic materials can be combined to form nanocomposites with different optical, catalytic and electrical properties [9, 10].

Among the nanocomposites, PANi–inorganic nanocomposites were concerned because of their applications in many industrial fields. The nanocomposites of polyaniline can be synthesized by polymerization of aniline in the presence of dispersed inorganic nanoparticles. This polymerization can be done by three various methods. One of them is the in situ chemical polymerization of aniline in an acidic solution with dispersion of inorganic nanoparticles in the presence of an oxidant at low temperature [11].

The properties of PANi can be tailored by changing its oxidation states, dopants or through blending it with other organic, polymeric or inorganic nanosized semiconducting particles [12].

 Co_3O_4 has the normal spinel structure of AB_2O_4 type. It is the traditional precursor of anode material in lithium ion rechargeable battery [13], supercapacitor [14] and catalyst for degradation of phenol, and removal of pollutants [15]. In bulk crystalline form, Co_3O_4 is antiferromagnetic while nanosized Co_3O_4 shows weak ferromagnetic or superparamagnetic properties [16]. Recently, it has shown that Co_3O_4 nanoparticles exhibit the bulk conductivity of $1.2W^{-1}cm^{-1}$ at room temperature [17].

Polyaniline and its nanocomposites have disadvantages such as low mechanical properties that makes thier use difficult in industry. There are several ways to fix the problem such as mixing of polyaniline or its nanocomposites with other polymers like epoxy resin or polyurethane to form a composition for casting or coatings.

Urethane acrylates (UA) were among the most important UV curable oligomers that show appropriate physical and mechanical properties such as flexibility, toughness, resistance and environmental stability [18-22], so the mechanical properties of polyanilines can be improved with the preparation of polyaniline and urethane acrylate composites. In this research, a novel UV curable conductive nanocomposite containing urethane acrylate and PANi- Co_3O_4 nanocomposite is prepared. This work is mainly focused on the effect of PANi- Co_3O_4 in urethane acrylate resin to prepare thin film UV curable conducting nanocomposite coating.

2. Experimental

2.1. Materials

Aniline, hydrochloric acid, ammonium peroxydisulfate $[(NH4)_2S_2O_8, (APS)]$, 1,6-hexanediol, isophorone diisocyanate (IPDI), 2-hydroxyl ethyl methacrylate (HEMA), dibutyltindilaurate (DBTDL), benzophenone and tripropylamine were purchased from Merck Company (Germany). Nano Co₃O₄ (30nm) was produced by US Research Nanomaterials, Inc (USA).

2.2. Characterization techniques

FT-IR spectra of the PANi and PANi-Co₃O₄ nanocomposites were recorded with Bruker Tensor 27 spectrometer in the region of 400-4000 cm-1 using KBr pellets. The optical absorption of nanocomposites in dimethyl sulfoxide (DMSO) solvent was measured at room temperature on UV-VIS spectrophotometer in the range of 200-800 nm. Electrical conductivity of pellets and films were measured with four point probe technique at room temperature. Pellets for measuring conductivity of the PANi and PANi-Co₃O₄ nanocomposites were prepared by a hydraulic compression-molding machine (the pressure of 1 ton). The surface morphology of the products was examined using scanning electron microscopy (LEO Company) operating at 10 kV.

2.3. Synthesis of polyaniline (PANi)

Polyaniline (PANi) was synthesized by oxidative polymerization method in the presence of ammonium persulphate ($(NH4)_2S_2O_8$) as an oxidant. At First, fresh distillated aniline (2 ml) in 100 ml of 1 M HCl solution at room temperature was stirred for 1h. Then 1M ammonium persulphate solution (40 ml) was added at the rate of 15 drops/min. After adding the whole solution of APS, the stirring was continued for 4.5h and temperature was maintained at 0°C and then mixture was kept overnight in the refrigerator to complete the reaction. The green precipitate was collected by filter and repeatedly rinsed with water and HCl solution .The product was dried in an oven at 70°C for 12h. Finally, the green precipitate of conducting form of polyaniline, emeraldine salt (ES), was obtained (Scheme 1).

2.4. Synthesis of PANi-Co₃O₄ nanocomposites

The PANi– Co_3O_4 nanocomposites were synthesized with different weight ratios (1, 2.5 and 5 %) of Co_3O_4 nanoparticles into PANi matrix (Scheme 2). Co_3O_4 nanoparticles (0.1g) were added to 0.24mol (2g) of aniline in aqueous acidic solution and then 1 M ammonium persulphate solution (40ml) was added slowly to the mixture. The reaction mixture was stirred for 6 hours at 0 °C in ice bath and then it was filtered. Obtained green precipitate was washed several times with distilled water, HCl solution and then it was dried. In a similar way, PANi–Co₃O₄ nanocomposites with different weights of Co₃O₄ nanoparticles (0.025, 0.05g) was prepared (Table 1). Scheme 2 shows the schematic representation of PANi-Co₃O₄ nanocomposites synthesis.



Scheme 1: reaction of PANi synthesis.

Table 1: Quantities of pure PANi and PANi- Co₃O₄ (1-5 wt %) nanocomposites.

Sample	Aniline (g)	Co ₃ O ₄ (g)	Co ₃ O ₄ in aniline(%)
PANi	2	0	0
PANi- Co ₃ O ₄ 1 wt%	2	0.025	1
PANi- Co ₃ O ₄ 2.5 wt%	2	0.05	2.5
PAN- Co ₃ O ₄ 5 wt%	2	0.1	5



Scheme 2: Suggested synthesis reaction of PANi-Co₃O₄ hybrid nanocomposite.

2.5. Synthesis of urethane acrylate (UA) oligomer

For preparation of a UV curable urethane acrylate resin, a prepolymer was first synthesised via the reaction of two equivalents (Eq) isophorone diisocyanateand one equivalent 1,6-hexanediol in the presence of few droplets of dibutyltindilaurate as catalyst and acetone (20 ml) as solvent in a 250 ml glass reactor that was equipped with a mechanical stirrer, condenser and inert gas line. In the next step, 2 equivalents hydroxyl ethylmethacrylate was added dropwise into the reactor for 30 min and then was stirred until the absorbance peak of -NCO group (2270 cm⁻¹) disappeared in FTIR spectra (Scheme 3). In the last step, the acetone was evaporated by vacuum pump.

2.6. Synthesis of UA-PANi-Co₃O₄ nanocomposites

Three different UA-PANi–Co₃O₄ nanocomposites were prepared using PANi–Co₃O₄ nanocomposites (1, 2.5, 5% Co₃O₄) in urethane acrylate matrix (Scheme 4).

10 g urethane acrylate and 0.1 g PANi–Co₃O₄ nanocomposites were mixed and stirred for 1h. Finally, 0.33 g benzophenone (initiator) and 0.33 g tripropylamine (co-initiator) were added and mixed for 10 minutes. UA-PANi nanocomposite was synthesized in the same method, but PANi was added into urethane acrylate.

2.7. Prepretion PUA-PANi-Co₃O₄ nanocomposites films

PUA-PANi and PUA-PANi- Co_3O_4 nanocomposites films were applied by film applicator on glass substrates with thickness of about 120 microns. Then, films were cured by UV radiation .



Scheme 3: Synthesis reaction of urethane acrylate (UA).

UA + PANi-Co₃O₄ $\xrightarrow{C_{13}H_{10}O}$ UA-PANi-Co₃O₄



3. Results and discussion

3.1. Fourier transform infrared (FTIR) analysis

PANi and PANi-Co₃O₄ nanocomposites were characterized by using FT-IR technique. Figure 1 shows the FT-IR pattern of PANi and PANi-Co₃O₄ nanocomposites. FT-IR spectrum of PANi (Figure 1a) shows all important absorption peaks at 3444, 2963, 2927, 1631, 1456, 1261, 1096 and 804cm⁻¹. The peak at 3444 cm⁻¹ corresponds to N–H stretching mode. The bands at 2963 and 2927 cm⁻¹ are due to aromatic C–H stretching vibrations. The bands at 1631 and 1456 cm⁻¹ are attributed to C=C stretching quinonoid and benzenoid rings of PANi, respectively. The peaks at

1261 and 1096 cm⁻¹ are assigned to C–N stretching mode of benzenoid ring. The band at 804 cm⁻¹ can be attributed to out-of-plane C–H bending [23-25].

The FT-IR spectrum for PANi–Co₃O₄ (5%) nanocomposite is shown in Figure 1b which shows some shift in the wavelengths and intensity of the peaks as compared to PANi. This indicates that the structural change of polymer occurs when Co₃O₄ nanoparticles are added to the PANi. The peak at 3443 cm⁻¹ can be associated to the interaction between Co₃O₄ nanoparticles and N–H group of PANi, so the peak displacement which was observed in FT-IR spectrum may be ascribed to the formation of hydrogen bonding between Co₃O₄ and the N–H group of PANi on the surface of the Co₃O₄ nanoparticles [26].



Figure 1: FT-IR spectra of (a) PANi (ES) and (b) PANi– Co₃O₄ (5 %) nanocomposite.

The bands at 2927 and 2870 cm^{-1} are due to aromatic C–H stretching. The bands at 1565, 1471 cm^{-1} may be attributed to C=C stretching quinonoid and benzenoid rings of PANi, while bands at 1293 and 1033 cm^{-1} are assigned to C–N stretching mode of benzenoid units. The band at 802 cm⁻¹ can be attributed to out-of-plane C–H bending.

The FT-IR spectrum for PUA and PUA-PANi– Co_3O_4 (5%) nanocomposite films is shown in Figure 2. The absorbance peak of -NCO group (2270cm⁻¹) disappeared in FT-IR spectrum. Figure 2a shows FTIR spectrum of PUA in which the peak at 3417cm⁻¹ is corresponding to N–H stretching. The bands at 2961 and 2924cm⁻¹ are due to CH₂ and CH₃ groups, respectively. The bands at 1638cm⁻¹ attribute to C=O group and the peaks at 1261cm⁻¹ are assigned to C–N stretching mode [20].

The FT-IR spectrum for PUA-PANi–Co₃O₄ (5%) nanocomposite shown in Figure 2b shows some shift in the wavelengths and intensity of the peaks as compared to PUA, which indicates that the structural change of polymer occurs when PANi–Co₃O₄ nanocomposite is added to the PUA. The peak at 3402cm^{-1} corresponds to N–H stretching. The bands at 2925 and 2854cm^{-1} are due to C–H stretching. The bands at 1744cm^{-1} are attributed to C=O group and the bands at 1580 and 1466cm^{-1} are ascribed to C=C stretching of PANi, respectively.



Figure 2: FT-IR spectra of a: PUA film and b: PUA-PANi–Co₃O₄ (5 %) nanocomposite film.

3.2. UV-VIS spectroscopy analysis

The UV–VIS absorption spectra of PANi (ES), PANi– Co_3O_4 hybrid nanocomposites recorded at room temperature are given in Figure 3.

In Figure 3a, we can observe two distinct peaks of polyaniline appear at about 267 and 388 nm which are attributed to π - π * conjugated ring systems, and π - π * transition of the benzenoid ring. UV–VIS spectra of

nanocomposites were almost similar to those of PANi and some shift in the bands was noticed.

Figure 3b shows UV–VIS spectrum of PANi– Co_3O_4 (5 %) hybrid in which two distinctive peaks at 272 and 390 nm are observed [27, 28]. The red shift of the absorption transition to higher wavelength was due to the interaction of Co_3O_4 nanoparticles with PANi matrix.



Figure 3: UV–VIS spectra of a: PANi and b: PANi- Co₃O₄(5 %) nanocomposite.

3.3. Morphologies of nanocomposites

The morphologies of PANi (ES) and PANi–Co₃O₄ (1– 5 wt %) nanocomposites are shown in Fig.4. The SEM image of polyaniline (Figure 4a1) exhibits clearly nanofibers with many pores and gaps among the fibers [29]. Figures 4a2–a4 show SEM images of PANi– Co₃O₄ hybrid nanocomposites (1–5 %). According to the SEM micrographs, PANi and Co₃O₄ nanoparticles have formed a nanocomposite in which the nanoparticles are embedded in the polymer matrix.

SEM images showed that the loading of Co₃O₄

nanoparticles have a powerful effect on the polyaniline's morphology, and a change in morphology of PANi is observed with increasing the amount of Co_3O_4 nanoparticles. It can be concluded for formation of hydrogen bonding between Co_3O_4 and the N–H group of PANi on the surface of the Co_3O_4 nanoparticles.

The morphologies of PUA-PANi and PUA-PANi- Co_3O_4 nanocomposites films are shown in Fig. 4b. The SEM images show that PANi– Co_3O_4 nanocomposites have been distributed in the urethane acrylate matrix.



Figure 4a: SEM images of a1: PANi (ES), a2-a4: PANi- Co₃O₄ (1, 2.5 and 5%) nanocomposites.



Figure 4b: SEM images of b1: PUA-PANi (ES), b2-b4: PUA-PANi- Co₃O₄ (1, 2.5 and 5% Co₃O₄) nanocomposites films.

3.4. Electrical conductivity

Table 2 shows the variation of conductivity of pure PANi and PANi-Co₃O₄ (1-5 wt % Co₃O₄) hybrid pellets. The conductivity nanocomposites measurements showed that the molecular chain contribution of polyaniline is the prominent carrier in nanocomposite. PANi-Co₃O₄ hybrid Electrical conductivity of PANi is 0.04 Ω^{-1} cm⁻¹ which decreased with increasing the Co₃O₄ nanoparticles in the PANi matrix. This can be attributed to the adsorption of NH of PANi on the surface of Co₃O₄ nanoparticles and bond formation and may be due to blocking of charge carriers. Additionally, increasing the amount of Co₃O₄ nanoparticles from 1 to 5 wt% decreased the electrical conductivity from 0.012 to 0.003 Ω^{-1} cm⁻¹. The reason is that with increasing the amount of Co_3O_4 nanoparticles, bond formation between NH of PANi with Co_3O_4 nanoparticles increases, hence the electrical conductivity of PANi– Co_3O_4 nanocomposites decreases [30, 31].

In fact, pure PANi is the most conductive sample and addition of the Co_3O_4 nanoparticles in the PANi matrix decreases the conductivity. The conductivity of Co_3O_4 nanoparticles at room temperature was 1.2 Ω^{-1} cm⁻¹ [17], but adding Co_3O_4 in the PANi matrix causes the decrease of PANi conductivity. It seems that the reason is the bond formation between NH of PANi with Co_3O_4 nanoparticles that due to decrease the conjugate chain length and blocking of charge carriers.

 Table 2: Conductivity of pure PANi and PANi–Co₃O₄ (1–5 wt %) nanocomposites pellets.

Sample	Conductivity (Ω^{-1} cm ⁻¹)(at 300K)
Pure PANi	0.04
PANi-1 wt%Co ₃ O ₄	0.012
PANi-2.5 wt% Co ₃ O ₄	0.010
PANi-5 wt% Co ₃ O ₄	0.003

Table 3. Conductivity of pure PUA and PUA-PANi- Co₃O₄ (1-5 wt %) nanocomposites films.

Sample	Co ₃ O ₄ particles (wt %)	Conductivity (Ω^{-1} cm ⁻¹)(at 300K)
Pure PUA	0	0.0001
PUA-PANi	0	0.0011
PUA-PANi-Co ₃ O ₄	1	0.0008
PUA- PANi- Co ₃ O ₄	2.5	0.0007
PUA-PANI- Co ₃ O ₄	5	0.0005

These charge carriers do not have sufficient energy to hop between favorable sites. Also, the decreased conductivity of PANi–Co₃O₄ nanocomposites may be ascribed to the behavior of Co₃O₄ in the nanocomposites or reduction of doping degree. The conductivity of the nanocomposites depends on the nature of dopant, the inorganic nanoparticles concentration and the length of the conjugate chain [32, 33].

Table 3 shows the variation of conductivity of pure PUA, and PUA-PANi-Co₃O₄ (1–5 wt % Co₃O₄) hybrid nanocomposites films. The results show that pure polyurethane acrylate film is almost non-conductive, but the conductivity of PUA films increases from 0.0001 to 0.0011 Ω^{-1} cm⁻¹ by addition of PANi and PANi-Co₃O₄. PUA-PANi is most conductive nanocomposites film (0.0011 Ω^{-1} cm⁻¹) because PANi is a conductive polymer (0.04 Ω^{-1} cm⁻¹). Also, the conductivity of PUA-PANi-Co₃O₄ films decreased (from 0.0008 to 0.0005) with increasing the amount of Co₃O₄ nanoparticles from 1 to 5 wt% due to bond formation between NH of PANi with Co₃O₄

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result, PUA-PANi film is the most conductive UV curable nanocomposite coating

4. Conclusions

Novel UV curable conductive nanocomposites containing urethane acrylate and PANi-Co₃O₄ nanocomposite have been prepared. At first, PANi-Co₃O₄ nanocomposites have been synthesized with different molar ratios of aniline: Co₃O₄ nanoparticles by in situ chemical oxidative polymerization method of aniline using ammonium persulphate as an oxidizing agent. Then PUA-PANi-Co₃O₄ nanocomposites films were prepared and curing of the films was completed by ultraviolet radiation. UV-VIS and FT-IR studies confirmed that there was strong chemical interaction between PANi and Co₃O₄ nanoparticles, which caused shifting of UV and FT-IR characteristic bands. The morphological studies of the PANi-Co₃O₄ nanocomposites showed uniform distribution of Co₃O₄ nanoparticles in PANi matrix, also SEM images of the PUA-PANi-Co₃O₄ nanocomposites films indicated distribution PANi-Co₃O₄ nanocomposites in PUA matrix. Electrical conductivity measurements of PANi-Co₃O₄ nanocomposites revealed that the conductivity of PANi decreased with addition of Co₃O₄ NPs. Results also showed that PUA-PANi film was the most

5. References

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conductive film and the conductivity of PUA increased in the presence of PANi and $PANi-Co_3O_4$ nanocomposites.

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